PROCESS FOR PREPARING 2,6-DIALKYLNAPHTHALENE

BACKGROUND OF THE INVENTION

SUB B1 >

1. Field of the Invention

The present invention relates to a process for producing and obtaining 2,6-dialkylnaphthalene (DAN), in particular 2,6-dimethylnaphthylene (2,6-DMN) from a mixture which contains at least one of dialkylnaphthalenes, monoalylnaphthalenes or naphthalene.

2. Discussion of the Background

The compound 2,6-DMN is used as a precursor of 2,6-naphthalene dicarboxylic acid in the manufacture of high performance polyester resins such as polyethylene naphthalate polymer (PEN) or polybutyrene naphthalate polymer (PBN), because 2,6-DMN is easily oxidized to 2,6-naphthalene dicarboxylic acid compared with other precursors such as 2,6-diisopropylnaphthalene or 2-methyl-6-isobutyrylnaphthalenes. There have been many expected PEN's applications to film and bottle uses, such as long time recording type video film, Advanced Photo System, hot fill containers, refillable bottles and tire codes because of its good physical properties in strength, thermal resistance and gas barrier property. Expected PBN's main applications are for electronics, insulators and car parts. However, PEN and PBN have heretofore been too expensive to expand its market cleanly because of few effective processes for the 2,6-DMN commercialization.

There have been many proposals concerning the process for preparing the 2,6-DMN.

U.S. Pat. No. 4,795,847 (Weitkamp et al.) describes a process for the preparation of 2,6-dialkylnaphthalene by alkylating naphthalene or 2-alkyl-naphthalene with an alkylating agent in the presence of a zeolite (specially ZSM-5) as a catalyst.

U.S. Pat. No. 5,001,295 (Angevine et al) describes a process for preparing DMN by using 2-monomethylnaphthalene (MMN) and naphthalene as a feedstock and a synthetic zeolite (MCM-22) as a catalyst, and it shows MCM-22 is more effective than ZSM-5 in alkylation of 2-MMN and naphthalene.

However these methods provide only unit operation (i.e batch) for alkylation of 2-MMN, which is an expensive feedstock and is not commercially available in a large amounts.

U.S. Pat. Nos. 4,990,717 (Sikkenga) and 5,073,670 (Sikkenga et al.) describes a multi-step process to produce 2,6-DMN from o-xylene and butadiene, which consists of;

1) preparation of 5-(o-tolyl)-pentene-2 (OTP) by alkenylation of o-xylene with butadiene in a presence of catalyst such as an alkali metal catalyst;

2) preparation of 1,5-dimethyltetralin (1,5-DMT) by cyclization of OTP in a presence of catalyst such as platinum and copper on an ultra stable zeolite catalyst;

3) preparation of 1,5-dimethylnaphthalene (1,5-DMN) by dehydrogenation of 1,5-DMT in a presence of catalyst such as platinum and rhenium and gamma alumina; and

4) preparation of DMN mixture which is rich in the desirable 2,6-DMN, 1,6-DMN and 1,5-DMN by isomerization of 1,5-DMN in a presence of catalyst such as a beta-zeolite catalyst.

If a 2,6-DMN separation from DMN mixture were combined with the above multi-steps, a complete process to produce purified 2,6-DMN could be provided.

As multiples steps makes a process plant complicate and in a high cost, it is hard to say that the prior art provides or a commercial process for an economical preparation of purified 2,6-DMN.

Furthermore, it is very difficult to separate 2,6-DMN from other isomers by conventional separation methods such as distillation and cooling crystallization because;

1) There are very small differences in boiling points of DMN isomers, especially the difference between 2,6-DMN and 2,7-DMN is only 0.3° C., where it is nearly impossible to separate 2,6-DMN by distillation.

2) The cooling of DMN isomer mixture solution of 2,6-DMN purification formes a precipitate of very fine 2,6-DMN crystals in suspension, where separation of the 2,6-DMN is extremely difficult.

Koide et al U.S. Pat. No. 4,992,619 reports a method of separating a methyl derivative of naphthalene from a mixture material in a high purity, by crystallization under a pressure.

Moritoki et al U.S. Pat. No. 4,784,766 reports a pressure crystallization apparatus.

Accordingly, method of commercially preparing dialkylnaphthalenes are sought.

SUMMARY OF THE INVENTION

According to one embodiment of the invention is a method of preparing 2,6-dialkylnaphthalene.

SUB B2 > According to another embodiment of the present invention is a method of preparaing 2,6-dimethylnaphthylene.

According to another embodiment of the present invention is a method of preparing a polyester resin.

SUB B3 > These and other objects of the present invention are made possible by a method of producing 2,6-dialkylnaphthalene from a feedstock which contains at least one component selected from the group consisting of dialkynaphthalene isomers, monoalkylnaphthalene isomers and naphthalene comprising the following steps:

I. separating a feedstock into a naphthalene, monoalkynaphthalene, dialkylnaphthalene fractions:

II. separating and purifying 2,6-dialkylnaphthalene from said dialkylnaphthlane fraction of step I;

III. alkylating said monoalkylnaphthalene fraction of step I with an alkylating agent to produce dialkylnaphthalene;

IV. transalkylating said naphthalene fraction of step I and a dialkylnaphthalene fraction, after 2,6-dialkylnaphthalene is separated therefrom in step II, to produce monoalkylnaphthalene, and isomers of dialkylnaphthalene.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same become better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1, illustrates a separation, purification and reaction scheme according to the present invention; and

FIG. 2, illustrates a separation, purification and reaction scheme wherein a dialkylnaphthalene fraction is enriched in 2,6-dialkylnaphthalene, according to the present invention; and

FIGS. 3, 4, 5, 6, 7, 8 and 9 illustrate separation, purification and reaction schemes according to preferred embodiments of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention may be applied to any feed streams of hydrocarbons that contains alkylnaphthalenes, at least one of naphthalene, MMN (monomethylnaphthalene) and DMN isomers including 2,6-triad DMN (2,6-DMN and/or 1,6-DMN and/or 1,5-DMN). In particular, LCO (Light Cycle Oil) from FCC (Fluid Catalyst Cracking) or HC (Hydrocracker) is a preferable example of a feed stream.

As for the separation of LCO into each fraction of naphthalene, MMN and DMN conventional method such as distillation can be utilized. However, LCO usually contains many kinds of components such as light paraffins and mono-aromatics with long chain alkyl-group, which have similar boiling points to boiling points of naphthalene, MMN and DMN (Co-boilers). It is very hard to separate alkylnaphthalenes from their co-boilers only by distillation.

In such case, they can be separated from their co-boilers by conventional solvent extraction method in step (I). However, this present invention, including utilization of MCM-22 catalyst charged in reactors (alkylator, transalkylator and isomerizer) can reduce the load of extraction or eliminate it. If hydrogen is co-fed to the reactors, MCM-22 catalyst can effect a cracking reaction to convert co-boiler components into components having a higher vapor pressure than each of naphthalene, MMN and DMN.

Therefore, as the co-boilers can be reformed and changed to components having a higher vapor pressure at the outlet of alkylator, transalkylator and isomerizer and the product from the reactors are recycled to step (I) Distillation, it is possible to perform further separation and concentration of each of naphthalene, MMN and DMN in step (I) as the preferable feed stream of each reactor.

Alternatively co-boilers may be reformed by a combination with a conventional hydrodealkylation technique. In this case, the following advantages can be achieved;

i) Co-boilers contained in the feedstock can be easily changed and it makes easier to separate them by distillation from naphthalenes, monoalkylnaphthalenes and dialkylnaphthalenes.

ii) Paraffins and mono-aromatics with long chains can be reformed to usefull BTX (benzene, toluene, xylene) or a gasoline fraction.

iii) Alkylnaphthalenes including polyalkylnaphthalenes, which are contained in the feedstock and/or which are formed by reactions (alkylation and/or transalkylation and/or isomerization), can be reformed to pure naphthalenes and monoalkylnaphthalenes, which are preferable feedstock for the reaction.

iv) In case the feed stream contains sulfur and nitrogen compounds, which might be catalyst poisons, these compounds can be excluded from the recycling streams and products.

Refinery plants usually have FCC or HC for gasoline recovery from residues of atmospheric distillation unit. LCO is a by-product and its main use is as a diluent of A-heavy oil and/or C-heavy oil by being mixed with them. Therefore, LCO is evaluated as having fuel value. However, LCO usually contains naphthalene and alkylnaphthalenes such as MMN and DMN fraction at about 20 to 35 weight %. (alkylnaphthalenes/LCO).

The present invention provides an effective production process of 2,6-DMN as high-value added product by utilizing a non valuable feed stream.

As a feed stream for the present process, any hydrocarbon feedstream containing at least one of naphthalene, MMN or DMN, such as Light Cycle Oil (LCO) derived from Catalytically cracking petroleum oil may be used.

For the separation and concentration of step (I), conventional techniques such as distillation can be applied to step (I) may be used. In the case were the feed stream contains non-aromatic components which boiling points are very similar to naphthalene and/or MMN, conventional solvent extraction techniques also can be applied in addition to the above mentioned distillation in step (I).

The conditions of alkylation include a temperature of about 0 to 500 ° C., and preferably 240 and 450 ° C., and a pressure of between 0 to 250 atmospheres and preferably 1 to 50 atmospheres. The mole ratio of alkylating agent to feed of monalkylnaphthylene or naphthalene can be from about 20:1 to 1:20, preferably from 10:1 to 1:10. The reaction is suitably accomplished utilizing a feed space velocity of about 0.1 to 10.0 hr^{-1}.

Preferred alkylating agents include alcohols, olefins, aldehydes, halides, and ethers. For example, methanol, dimethylether and polyalkylbenzene are preferred. Methanol and dimethylether are especially preferred.

A suitable catalyst for alkylation, is a synthetic zeolite characterized by an X-ray diffraction pattern including interplanar d-spacing and relative intensity $I/I_o \times 100$

12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06Å	VS.

A suitable catalyst is described in U.S. Pat. No. 5,001,295, as MCM-22.

The alkylation can be carried out in any of the known reactors usually employed for alkylation. For example, a tubular reactor with a downflow of reactants over a fixed bed of catalyst can be employed.

The conditions of transalkylation include a temperature of about 0 to 500° C., and preferably 200 to 450° C., and a pressure of 0 to 250 atmospheres and preferably 1 to 25 atmospheres. The mole ratio of naphthalene to DMN can be from about 10:1 to 10, preferably from 5:1 to 1:5. The reaction is suitably accomplished utilizing a feed space velocity of about 0.1 to 10.0 hr^{-1}.

A suitable catalyst for transalkylation, is a synthetic zeolite characterized by an X-ray diffraction pattern including interplanar d-spacing and relative intensity $I/I_o \times 100$

12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06Å	VS.

A suitable catalyst is described in U.S. Pat. No. 5,001,295, as MCM-22.

Separation of 2,6-dialkylnaphthalene maybe conducted by conventional methods of separation known to those of ordinary skill in the art such as cooling crystallization or adsorption. For example separation may be affected by using a method of crystallization under high pressure. In general,

a liquid mixture containing two or more substances is pressurized, and a certain substance in the mixture is solidified and separated from the residual liquid by the effect of the pressure. In other words, this method involves a separating and purifying technique wherein a liquid mixture containing two or more substances is placed in a tightly sealed pressure vessel, a portion of the desired substance, 2,6-dialkylnaphthalene, is solidified to form a solid-liquid co-existing state, the liquid is discharged from the co-existing system while maintaining the pressure of the solid-liquid co-existing system at a higher level than equilibrium pressure of the objective substance, then the solid remaining in the vessel is pressed for discharging the residual liquid between the solid particles and integrating the solid particles. This technique is generally described in U.S. Pat. No. 5,220,098.

SUB B5 > The method involves injecting the slurry or liquid of the temperature of 70 to 120° C., preferably 80 to 100° C., into a high pressure vessel for conducting a crystallization under high pressure; adiabatically pressurizing the vessel to a pressure of from 300 to 4,000 kgf/cm^2, preferably 500 to 2,000 kgf/cm^2 to increase the quantity, i.e. the amount of 2,6-dialkylnaphthalene crystals, whereby coexistence of solid-liquid phases exist at the high pressure conditions; discharging the liquid phase component from the high pressure vessel, the discharging being conducted under pressure, to increase the ratio of the solid phase relative to the liquid phase within the vessel; lowering the pressure of the residual liquid phase so as to dissolve partially and purify the product; discharging the residual liquid phase by applying pressure to the solid phase within the high pressure vessel whereby a 2,6-dialkylnaphthalene crystal block having a high purity is obtained within the high pressure vessel. By this technique, a purity of 2,6 dialkylnaphthalene (e.g. 2,6-dimethylnaphthylene) of ≧98% by weight, preferably ≧99% by weight may be obtained.

In a preferred embodiment, a 2,6-lean dialkylnaphthalene fraction may be subject to isomerization conditions to provide for a dialkylnaphthalene fraction which has a greater content of 2,6-dialkylnaphthalene.

Isomerization conditions are those generally as disclosed in co-pending application U.S. Pat. No. 08/661,114, as suitable for conducting simultaneous transalkylation of dialkylnaphthalene and naphthalene, and isomerization of dialkylnaphthalenes, the relevant portions of which are hereby incorporated by reference.

As a suitable catalyst for isomerisation, a synthetic zeolite characterized by an X-ray diffraction pattern including interplanar d-spacing and relative intensity I/I_o100

12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06Å	VS.

A suitable catalyst is described in U.S. Pat. No. 5,001,295, as MCM-22, the entire contents of which are hereby incorporated by reference.

Preferably, isomerization is conducted at a weight hourly space velocity (WHSV) of dialkylnaphthalenes of 0.1 to 10, preferably 0.5 to 5 h^{-1}, more preferably 0.75 to 1.5 h^{-1}.

Preferably, isomerization is conducted at a temperature of from 100 to 500° C., preferably 150 to 350° C., more preferably 200 to 300° C.

Preferably, isomerization is conducted at a pressure of atmospheric to 100 kgf/cm^2, preferably atmospheric to 30 kgf/cm^2.

During isomerization it is possible to co-feed of hydrogen, but is not always necessary, in an amount of 0.1 to 10 mol-H_2/mol-hydrocarbons.

The resulting 2,6-dialkylnaphthalene, e.g. 2,6-dimethylnaphthalene may then be used to produce a polyester resin, by oxidation of 2,6-dimethylnaphthalene to form 2,6-naphthalenedicarboxylic acid, by conventional methods known to those of ordinary skill in the art.

The 2,6-naphthalenedicarboxylic acid may then be condensed with a diol such as ethylene glycol, propylene glycol, butane diol, pentane diol and hexane diol. In a preferred embodiment, the polyester resin formed in a polyethylenenaphthalate or polybutylenenaphthalate resin. Such a condensation may be conducted by conventional methods known to those of ordinary skill in the art.

Alternatively a polyester resin may be formed from 2,6-naphthalenedicarboxylic acid by first esterification of 2,6-naphthalenedicarboxylic acid with an alcohol such as a C_{1-6} alcohol, such as methanol, ethanol, propanol, isopropanol, n-butanol, s-butanol, i-butanol, t-butanol. In a preferred embodiment, the alcohol is methanol. Esterification may be conducted by conventional techniques known to those of ordinary skill in the art. The alkylester of 2,6-naphthalenedicarboxylic acid by then be condensed with a diol as described above, by conventional methods known to those of ordinary skill in the art. Suitable diols include ethylene glycol, propylene glycol, butane diol, pentane diol and hexane diol. In a preferred embodiment the diol is either ethylene glycol or butane diol.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES

Example 1 Alkylation of MMN and Naphthalene:

A 153 g amount of MCM-22 is charged into a tubular reactor (volume:370 cc). As a feedstock for alkylation, 1-MMN, 2-MMN and naphthalene are used, and mixed at a molar ratio of 2.2 of 2-MMN/1-MMN, and a weight ratio of 3.0 of MMNs (1-MMN+2-MMN)/naphthalene.

Thereupon, the feedstock is supplied to the reactor (254° C., 5 kg/cm^2) at a rate of 153.4 g/hr and 1.0 hr^{-1} in WHSV with a feed of hydrogen at the rate of 1.8 ft^3/hr. Four hours later, methanol, as an alkylating agent, is introduced into the reactor at 35.5 g/hr, and alkylation is conducted for 20 hours. The product obtained is analyzed by gas chromatography, and the results are summarized in Table 1.

TABLE 1

Alkylation of Monomethylnaphthalene and Naphthalene

Component (wt %)	before reaction	after reaction
dimethylnaphthalene	0	17.19
2,6-DMN	0	1.72
2,7-DMN	0	1.20
other isomers	0	14.27
monomethylnaphthalene	73.63	60.10
2-MMN	50.55	40.32
1-MMN	23.08	19.78

TABLE 1-continued

Alkylation of Monomethylnaphthalene and Naphthalene

	before reaction	after reaction
naphthalene	25.28	18.67
other component	1.00	3.91
evaluation		
NL conversion (%)	—	26.15
2-MMN/1-MMN	2.2	2.04
MMN conversion (%)	—	18.37
2,6-DMN/total DMN (%)	—	10.02
2,6-DMN/2,7-DMN	—	1.44

As can be seen from Table 1, the ratio of 2,6-DMN/2,7-DMN is over 1.1 and the ratio of 2-MMN/1-MMN is over 2.0.

Example 2 Transalkylation:

A 30 g amount of MCM-22 (1/16" D×3/8"L, cylindrical pellet) are charged into a tubular reactor (volume: 122 cc). The reactor is heated from room temperature to 400° C. at the rate of 100° C./hr while introducing nitrogen gas into the reactor at atmospheric pressure.

As a feedstock for transalkylation, isomers of DMN and naphthalene are mixed in a molar ratio of 5:1. Feedstock and product analysis are shown in Table 2.

TABLE 2

Transalkylation and Isomerization

	before reaction	after reaction
Component (wt %)		
dimethylnaphthalene	84.37	65.91
2,6-DMN	5.22	11.39
2,7-DMN	7.28	7.42
other isomers	71.87	47.10
monomethylnaphthalene	0.17	13.81
2-MMN	0.02	9.54
1-MMN	0.15	4.27
naphthalene	15.46	12.65
other component	0	7.63
evaluation		
2,6-DMN/total DMN (%)	6.2(1)	17.3(2)
2,6-DMN/2,7-DMN	0.72	1.53
content of 2,6-DMN (after/before): @1	—	2.79
NL conversion (%)	—	18.2
DMN conversion (%)	—	21.9
produced MMN/(converted DMN × 2): @2	—	0.41
2-MMN/1-MMN	—	2.2

@1 The ratio of (2)/(1) in 2,6-DMN/total DMN
@2 Amounts are calculated on a molar basis.

As can be seen from Table 2, the ratio of 2,6-DMN/2,7-DMN is over 1.2 and the ratio of 2-MMN/1-MMN is over 2.0.

Example 3 Isomerization:

A 25 g amount of MCM-22 is charged into the tubular reactor (volume: 200 cc). The reactor is heated gradually from ambient temperature to 400° C. to dry the catalyst while supplying nitrogen gas, and the flow of nitrogen gas is ceased when the temperature becomes stable at 400° C. Thereupon, 2,6-lean-DMN is supplied to the reactor at the rate of 25 g/hr and 1.0 hr^{-1} in WHSV, and isomerization of DMN is carried out for four hours. The contents of the obtained product are analyzed by gas chromatography, and the results are summarized in Table 3.

TABLE 3

Isomerization

	before reaction	after reaction
Component (wt %)		
dimethylnaphthalene	98.09	80.10
2,6-DMN	6.21	13.96
2,7-DMN	8.48	8.66
other isomers	83.40	57.48
monomethylnaphthalene	0.20	9.77
2-MMN	0.03	6.71
1-MMN	0.17	3.06
naphthalene	0	0.78
other component	1.71	9.35
evaluation		
2,6-DMN/total DMN (%)	6.3	17.4
2,6-DMN/2,7DMN	0.73	1.61

As can be seen from Table 3, the ratio of 2,6-DMN/2,7-DMN is over 1.1.

Example 4 Separation of Purification:

(1) Crystallization under High Pressure Crystallization

A 1,505 g amount of DMN isomers is supplied into the high pressure crystallizer (KOBELCO 1.5 L type), and 236 g of 2,6-DNN crystals (purity 87%) are separated under the condition of 2,000 kgf/cm^2 and 45° C.

(2) Cooling Crystallization

Using a vessel for crystallization (3 liter), 2,001 g of DMN isomers is cooled quickly from 50° C. to 40° C. with slow stirring. Then, 0.5 g of seed crystals are charged to the vessel which is kept at a temperature at 40° C. for an hour. Thereupon, the feedstock is cooled to 10° C. at 2° C./min. A 360 g amount of 2,6-DMN crystals (purity 68%) is separated by filtration under pressure.

The results of separation by both crystallization under high pressure and cooling crystallization are summarized in Table 4.

TABLE 4

Separation

Component (g)	before crystallization	crystal	filtrate
CRYSTALLIZATION UNDER HIGH PRESSURE			
2,6-DMN	301	205	96
2,7-DMN	232	22	210
other DMN	972	9	963
TOTAL	1505	236	1269
2,6-DMN/2,7-DMN	1.3	—	0.5
2,6-DMN/total DMN	20.0%	—	7.6%
purity of crystal	—	87%	—
recovery of 2,6-DMN	—	68%	—
yield of 2,6-DMN	—	13.6%	—
COOLING CRYSTALLIZATION			
2,6-DMN	400	244	156
2,7-DMN	308	67	241
other DMN	1293	49	1244
TOTAL	2001	360	1641
2,6-DMN/2,7-DMN	1.3	—	0.65
2,6-DMN/total DMN	20.0%	—	9.5%